APPENDIX F
CONSIDERATION OF TOTAL PETROLEUM HYDROCARBONS WITHIN THE MRBCA PROCESS

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F.1 INTRODUCTION

Petroleum compounds contain a mixture of several hundred chemicals ranging from light, volatile, short chained organic compounds to heavy, long chained, branched compounds. These various compounds exhibit a range of physical, chemical, and toxicological properties. However, the properties of several of these compounds are not known and, therefore, calculating risk-based target levels for them is not possible. Further, analyzing the concentration of each of these compounds in the environmental media affected by a petroleum release is not practical. Thus a variety of methods have been developed to identify key constituents of the products and to estimate media-specific target levels for these constituents. These methods include:

1. Development of target levels for total petroleum hydrocarbons (TPH),
2. Development of target levels for specified ranges of petroleum hydrocarbons, e.g. TPH-GRO (gasoline range organics), TPH-DRO (diesel range organics), and TPH-ORO (oil range organics),
3. Development of target levels for a few constituents, (those considered most toxic and for which sufficient data are available), e.g. benzene, toluene, ethylbenzene, xylenes, naphthalene, and polynuclear aromatic hydrocarbons (PAHs),
4. Development of target levels for a specified size range of aromatic and aliphatic fractions, e.g. aliphatics >C6-C8, aliphatics >C8-C10, aromatics >C10-C12, etc., and
5. A combination of the above approaches.

MDNR has determined that petroleum hydrocarbon impacts will be evaluated using the following approach:

- Depending on the product released, indicator chemicals (i.e., chemicals of concern or COCs) will be selected from Table 5-1 and analyzed using the method indicated in Table 5-1.
- All soil and groundwater samples will be analyzed for TPH-GRO using SW-846 Method 8260 and for TPH-DRO and TPH-ORO using SW-846 Method 8270.
- If the product released is not known, the relative concentrations of TPH-GRO, TPH-DRO, and TPH-ORO can be used to identify the product that has been released and to select the relevant COCs from Table 5-1.

As appropriate on a case-by-case basis and as further discussed in section F.4 below, selected samples may also be analyzed for specified petroleum carbon fractions. Site-specific application of this method requires pre-approval by MDNR.

F.2 DEVELOPMENT OF TARGET LEVELS FOR TPH-GRO, TPH-DRO, AND TPH-ORO

As mentioned in Section 6.2, development of target levels requires the following information:

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Deleted: Each of the above methods results in target levels that approximately represent the risks of the various petroleum products. However, in each case, the field sampling and laboratory analysis method should be consistent with the method used to develop the target levels being considered. For example, if target levels are developed for specific aromatic and aliphatic fractions (method 4 above), soil and groundwater samples should be analyzed for the corresponding fractions. Note that the laboratory analysis costs for measuring TPH concentrations are significantly lower than for measuring individual petroleum fractions. Therefore, the selection of a particular method can have significant cost implications. If cost were not an issue, measurement of individual fractions (approach 4) would be the most appropriate method for developing target levels.¶
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Within the MRBCA process,

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Deleted: The remaining portion of this appendix describes the data used to develop target levels for TPH-GRO, TPH-DRO, TPH-ORO, and individual petroleum fractions. ¶

- Target risk level for carcinogenic and non-carcinogenic adverse health effects. For specific discussion, refer to Section 6.2.1 and Appendix B.1. Note that, currently, TPH-GRO, TPH-DRO, and TPH-ORO fractions are evaluated for non-carcinogenic effects only.
- Quantitative toxicity values for each fraction range. These are presented in Table B-1 and discussed in Section 6.2.2 and at B.2 of Appendix B.
- Fraction-specific physical and chemical properties. These are presented in Table B-2 and discussed in Section 6.2.5 and at B.3 of Appendix B.
- Receptor-specific exposure factors. These are presented in Table B-3 and discussed in Section 6.2.3 and at B.4 of Appendix B.
- Fate and transport parameters. These are presented in Table B-4 and discussed in Section 6.2.4 and at B.5 of Appendix B.
- Intake equations and fate and transport models. For specific discussion, refer to Section 6.2.6 and at B.6 of Appendix B.

The overall approach for developing target levels for each petroleum fraction is the same as that described in Appendix B, except for the chemical-specific properties discussed below.

F.2.1 Toxicological Properties of Various Fractions

Table B-1 lists the toxicological properties of the petroleum fractions that are necessary to develop target levels for TPH-GRO, TPH-DRO, and TPH-ORO. These values have been obtained from Toxicity Factors Table for Texas Risk Reduction Program Rule (March 31, 2003).

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F.2.2 Physical and Chemical Properties of Various Fractions

Table B-2 lists the chemical-specific properties of the petroleum fractions that are necessary to develop target levels for TPH-GRO, TPH-DRO, and TPH-ORO. These values have been obtained from Chemical/Physical Properties Table for Texas Risk Reduction Program Rule (March 31, 2003).

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F.2.3 Development of Target Levels

Table F-1 lists the aromatic and aliphatic fractions included in the TPH groups TPH-GRO, TPH-DRO, and TPH-ORO. These fractions are consistent with the chosen analytical methods, though they may not be consistent with other methods used to analyze TPH-GRO, TPH-DRO, and TPH-ORO. Therefore, for TPH analyses, consultants and laboratories should use Methods 8260 and 8270 and the ranges specified in this document.

Risk-based target levels for TPH-GRO, TPH-DRO, and TPH-ORO are developed using the following steps:

Step 1: Calculate target levels for individual TPH fractions within the group. These fractions are listed in Table F-1. (Each TPH fraction is treated as an individual chemical and the computation software is set up to calculate target levels for each fraction.)

Step 2: Add the target levels calculated at Step 1 for each fraction within a TPH group to obtain the target level for that particular TPH group.

Step 3: In Step 1, if the target levels for all the fractions within a particular TPH group exceeded the theoretical maximum concentration (soil saturation for soil and solubility for groundwater), the target level calculated in Step 2 for that particular group is assumed to exceed the theoretical maximum concentration.

The computation software performs the above steps so that TPH-GRO, TPH-DRO, and TPH-ORO target levels as well as the levels for individual fractions will be generated and displayed. The calculated Tier 1 target levels are tabulated in Tables 7-1 through 7-6(c).

F.3 SITE-SPECIFIC IMPLEMENTATION OF THIS APPROACH

For Tier 1 and Tier 2 evaluations, the evaluator should collect and analyze soil and groundwater samples to determine the concentrations of the three TPH groups using Method 8260 for TPH-GRO and Method 8270 for TPH-DRO and TPH-ORO. Samples should be analyzed using the methods indicated in Table 5-1. Since the measured value of TPH-GRO includes the concentration of BTEX, the total BTEX concentration should be subtracted from the TPH-GRO concentration prior to comparing the TPH-GRO value with Tier 1 and Tier 2 target levels. This correction will ensure that comparison of the measured and target values are consistent with the assumptions used to estimate the Tier 1 and Tier 2 target levels. The measurement of TPH-GRO, TPH-DRO, and TPH-ORO may also be affected by the presence of polar compounds naturally present in the subsurface (e.g. leafwax and biodegradation products such as carboxylic acids). If possible, these polar compounds should be removed prior to analysis using a silica gel or alumina column.

For Tier 3 risk assessment, the person performing the MRBCA evaluation may either compute target levels for (i) the three TPH fractions, or (ii) individual aromatic and aliphatic carbon fractions listed in Table F-1. If the latter approach is used, soil and groundwater concentrations shall be analyzed using Methods 8260 and/or 8270.

F.4 Analysis of Specified Petroleum Carbon Fractions

Petroleum carbon fraction analysis is a Tier 3 activity and shall be by Texas Natural Resource Conservation Commission (TNRCC) Method 1006[1] or another method approved by the Department.

Analytical methods are available to identify and quantify the specific petroleum carbon fractions listed in Table F-1 of this appendix. The resulting data can be useful in characterizing the type of petroleum detected; evaluating compositional changes due to chemical, physical, and biological attenuation processes; and assessing risk.

[1] TNRCC Method 1006 may not be used for the analysis of individual chemicals of concern other than carbon fractions. Individual chemicals of concern shall be analyzed by the methods listed in Table 5-1 of this guidance.

Table F-1
Constituent Fraction of TPH Groups

TPH Group	TPH Fractions	
	Aliphatics	Aromatics
TPH-GRO	>C6-C8 >C8-C10	>C8-C10
TPH-DRO	>C10-C12 >C12-C16 >C16-C35*	>C10-C12 >C12-C16 >C16-C21*
TPH-ORO	>C16-C35*	>C21-C35*

* The fate and transport and toxicity properties of the aliphatic fraction >C16-C35 used in the DRO calculation are identical to the properties of the aliphatic fraction >C16-C35 used in the ORO calculation. Likewise, the properties of the aromatic fraction >C16-C21 used in the DRO calculation are identical to the properties of the aromatic fraction >C21-C35 used in the ORO calculation. The target levels for these aliphatic and aromatic fractions are identical.

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